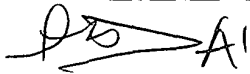


WO 01/18129

PCT/EP00/08211

Mixer system for preparing water-thinnable coating compositions



The subject matter of the present invention is a mixer  
5 system for preparing water-thinnable coating  
compositions with precisely defined tinting from  
different base colors. The present invention also  
relates to a process for preparing these coating  
compositions with precisely defined tinting, in which  
10 different base colors are stored separately and only  
shortly before application are mixed to give the  
coating composition in the desired shade.

The present invention further relates to the use of the  
15 mixer system for preparing aqueous basecoat materials  
for coating automobile bodies and/or plastic parts, and  
also for preparing aqueous coating compositions for  
refinish.

20 Customary methods of repairing damaged areas on a  
possibly multicoat paint system comprise careful  
cleaning and sanding, optional filling and surfacing  
the damaged area. The damaged area is then, possibly  
following further pretreatment, sprayed with effect  
25 paints, such as metallic basecoat materials, or with  
solid-color paints, normally hidingly and running out  
into the adjacent areas. After the coating produced in  
this way has been subjected to an initial drying, the

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coating and the adjacent parts are oversprayed with a clearcoat material and, after any flashoff time that may be needed, the clearcoat is dried together with the previously applied films at temperatures, preferably,  
5 of between 50 and 100°C.

Effect paints and/or solid-color paints applied in the two-coat method which are used for repairing damaged areas are normally low-solids paints which, in addition to binders, include color and/or effect pigments and a  
10 high fraction of organic solvent mixtures.

These paints either are supplied by the paint manufacturer in the desired shade, or the shade is produced prior to application from a mixer system of  
15 two or more base colors. This preparation from a mixer system has the advantage that there is no need to prepare and stock every shade individually and that it is therefore possible to reduce production, distribution, and warehousing costs. In both cases it  
20 is necessary for the paints supplied to have a sufficient shelf stability (at least 12 months). For a mixer system, furthermore, the shade accuracy of the base colors is of great significance.

25 Whereas in OEM finishing the use of water-thinnable basecoat materials is on the increase, it is still conventional, i.e., solventborne, basecoat materials that are used in the field of automotive refinish. These low-solids basecoat materials used hitherto for

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refinish have a composition which is distinctly different than that of the water-thinnable basecoat materials used hitherto for OEM finishing. For example, in the conventional systems, rheology control is effected for the most part by way of the evaporation rate of the organic solvents (increase in solids between application equipment and object to be coated), whereas in the case of the aqueous systems rheology control takes place by means of external thickeners or by means of corresponding modifications in the binder. For the transition from conventional to water-thinnable systems, therefore, the mere replacement of the binders used by water-dilutable binders is not enough.

The use in the refinish field of the water-thinnable systems used in the field of OEM finishing is also not possible at the present time owing to the different requirements imposed on the systems in the two fields. The water-thinnable metallic basecoat materials used for OEM finishing (original vehicle finishing), in fact, do not have a shelf life which is sufficient for the refinish field, since with these water-thinnable paints problems occur in terms of gas instability (formation of  $H_2$  as a result of reaction between water and the aluminum bronze) and/or effect stability. Both have a sustained adverse effect on the color shade of the resultant coatings and their brightness when viewed straight on. Consequently, these systems have not been employed in refinish.

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However, it is not only water-thinnable paints containing effect pigments that show problems in terms of shelf stability. Color pigments too can be attacked by prolonged exposure to water, e.g., in an alkaline  
5 medium. So that the restrictions on selection of commercially customary pigments are not too great, there is also a need for the formulation of storage-stable base colors containing these color pigments.

10 For economic reasons, for improving workplace safety (fire protection), and for reducing the environmental burden during the drying of the paint films, efforts are also being made in the refinish field to reduce organic solvents in the coating compositions as far as  
15 possible. The deficient shelf stability of the known water-thinnable basecoat materials, however, has so far prevented the construction of a mixer system as described above from water-thinnable basecoat materials of this kind.

20

EP-A-320 552 discloses a process for producing a multicoat coating system, in which the substrate, which has been provided with a surface layer, is first of all coated with an aqueous coating composition, preferably  
25 one comprising metallic pigments, and is dried before a customary aqueous basecoat material and then a clearcoat material are applied. As a result of the application of the aqueous coating composition prior to the basecoat/clearcoat system, it is intended that an

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improvement is achieved in the metallic effect, especially the straight-on brightness.

This process described in EP-A-320 552 is suitable primarily for the production of an original finish,  
5 although the description does note the possibility of using this process in the refinish field as well.

The aqueous coating compositions used in the process of EP-A 320 552 are prepared by incorporating an aluminum  
10 pigment paste into aqueous mixing varnishes. The aluminum paste used represents a pasted mass of aluminum bronze in organic solvents, and an emulsifier. This aluminum paste, however, settles within just a few hours and so leads to a sediment. This in turn,  
15 however, leads regularly to deviations in shade. This settled paste can be reagitated only to a certain extent using appropriate stirring units. Moreover, painters do not generally have such stirring equipment available. Aluminum pastes of this kind are therefore  
20 not suitable for constructing mixer systems for refinish.

In addition, the aqueous coating compositions obtained after the aluminum paste has been incorporated into the  
25 aqueous mixing varnishes exhibit inadequate shelf stability, which does not satisfy painter requirements.

Furthermore, EP-A-195 931 and EP-A-297 576 disclose aqueous coating compositions for producing a multicoat

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system in the OEM finishing field. The aqueous coating compositions are prepared by incorporating a pigment paste into the aqueous binder dispersion. The pigment paste is prepared by grinding the corresponding pigments with very small amounts of a grinding resin and, where appropriate, with organic solvents and, where appropriate, with water. The construction of a mixer system for the refinish field, and the measures necessary for this purpose, such as, for example, the separate storage of individual components, however, are not described in EP-A-195 931 and EP-A-297 576. Owing to the inadequate shelf stability, the pigmented aqueous coating compositions themselves are unsuited to the refinish field.

EP-B-38 127 also discloses aqueous coating compositions for producing a multicoat system in the OEM finishing field. The aqueous coating compositions are prepared, again, by incorporating a pigment paste into the aqueous binder dispersion. The pigment paste is obtained by grinding the pigments with a melamine resin and with organic solvents. The construction of a mixer system for the refinish field, and the measures necessary for this purpose, are again not described, however. These pigmented aqueous coating compositions of EP-B-38 127 are also unsuited to the refinish field, owing to inadequate shelf stability.

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EP-A-368 499 describes water-thinnable coating materials, comprising metallic pigments in particular, which feature improved shelf stability. This shelf stability is achieved by first preparing a water-free  
5 binder solution from 25 to 95% by weight of a polyetherpolyol or polyesterpolyol, 2.5 to 50% by weight of an amino resin, and 0 to 50% by weight of an organic solvent, and incorporating the pigments into this solution. Shortly before application, this binder  
10 solution is adjusted to the particular desired viscosity with water. EP A-368 499 does not describe the use of the water-free binder solutions in a mixer system. Furthermore, use of the coating materials of EP-A-368 499 under refinish conditions is impossible,  
15 since the high polyether/polyester fraction does not result in sufficiently water-resistant films. Furthermore, the metallic effect achieved is far short of that sufficient for automotive OEM or refinish painting.

20 Finally, the journal article by Hauska and Racz in Farbe und Lack, vol. 93, No. 2, 1987, pages 103 to 105 discloses improving the shelf stability of aqueous paint dispersions by measures including the use, for preparing the aqueous paint dispersions, of aluminum  
25 pastes containing not only aluminum pigment but also a binder which is miscible with the aluminum pigment and can be diluted with water before use. The binders specified in this journal article for preparing the aluminum paste, however, are not suitable for use in

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aqueous coating materials for the automotive refinish field. Accordingly, it is noted in the journal article itself that this method has no industrial significance. Nor does this journal article describe the construction  
5 of a mixer system or the measures necessary for this purpose.

Additionally, EP-A-0 468 293 and EP-A-0 471 972 describe aqueous paints based on different building  
10 blocks. It is, however, necessary for the effect building block to be water-free.

DE-A-41 10 520 describes a mixer system said to be suitable for preparing aqueous pigmented coating  
15 compositions with precisely defined tinting. In particular, it is said that aqueous basecoat materials are prepared using it. The mixer system is composed of different base colors (A) which contain less than 5% by weight of water, are preferably water-free, and contain  
20 pigments, solvents, and water-dilutable binders, and of a pigment-free aqueous component (B) containing, in particular, water-dilutable binders and/or rheological additives.

25 EP 0 608 773, finally, discloses a process for preparing aqueous coating compositions, particularly for preparing aqueous one-component effect basecoat materials of low solvent content using a modular system or mixer system or building block system which has



shelf stability over long periods, the individual modules of the system being easy to mix with one another in order to achieve a desired effect. In this case, a modular system containing an effect module with  
5 a high water content of at least 20% is used.

The object on which the present invention is based, accordingly, is to provide a mixer system which allows the preparation of water-thinnable coating compositions  
10 with precisely defined tinting from different base colors. In particular, this mixer system ought to allow the preparation of aqueous coating compositions suitable for refinish, especially the refinish of damaged areas on automobile bodies. High shade accuracy  
15 of the base colors ought to be ensured, in order to be able to set the desired shades without cumbersome painter measures in a way which is as reproducible and precise as possible. This also means that the base colors used to construct this mixer system are required  
20 to have a very good shelf stability (> 12 months).

Finally, the aqueous coating materials prepared using this mixer system, in the case both of effect paints and of straight shades, ought to give coatings having good mechanical properties.

25

This mixer system ought to ensure the formulation of coating compositions which ensure this high quality level with an organic solvent fraction which is reduced in comparison to the coating compositions commonly

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prepared. The mixer system in question is a mixer system for preparing water-thinnable coating compositions with precisely defined tinting from different base colors, the mixer system comprising

- 5 A) different base colors A containing water,  
Aa) from 0.5 to 70% by weight of at least one color and/or effect pigment,  
Ab) from 10 to 80% by weight of at least one water-dilutable or water-dispersible binder  
10 which can be prepared in the form of organic solutions, and  
Ac) one or more organic solvents and, where appropriate, auxiliaries and additives, the sum of the weight fractions of components Aa)  
15 to Ac) being in each case 100% by weight, and
- B) at least one water-containing, pigment-free component B which comprises at least one rheology control additive and also, where appropriate, at  
20 least one water-dilutable or water-dispersible binder, and, where appropriate, further auxiliaries and additives.

This object is at least achieved in that the water  
25 content of component A is 5% by weight and less than 20% by weight. The water content is preferably 6-19% by weight, most preferably from 8 to 16% by weight.

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Subject matter of the present invention is also a process for preparing water-thinnable coating compositions with precisely defined tinting, in which different base colors of a mixer system are prepared  
5 and stored separately and are not mixed until shortly before the application of the coating composition, characterized in that the mixer system of the invention is used.

10 Finally, the present invention also relates to the use of the mixer systems for preparing aqueous coating compositions for refinish, especially for preparing aqueous basecoat materials for refinish, particularly that of automobile bodies.

15 It is surprising and was not foreseeable that the mixer system of the invention allows the preparation of aqueous coating materials which feature a precise and reproducible establishment of the desired color shade without the need for laborious measures for this  
20 purpose. It is ensured by a high shade accuracy and a correspondingly good shelf stability of the base colors. A further advantage is to be seen in the fact that the base colors prepared in accordance with the invention are insensitive to freezing/thawing.

25 Furthermore, the aqueous coating materials thus prepared have the advantage that they lead to coatings having good mechanical properties. The paints are more environmentally friendly than the conventional water-free systems.

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A further advantage is that, as a result of the mixer system of the invention, the refinish field as well is one in which coating compositions are made available which meet the high requirements imposed for quality of the refinish and for that purpose contain predominantly water as the solvent, containing only small amounts of organic solvent. Besides economic advantages, this reduced solvent fraction leads to an improvement in workplace safety (fire protection) and to a reduction in the environmental burden associated with drying of the paint films. This is of importance in particular in the field of the refinish of automobile bodies, since the effect paints used in this field commonly include a very high solvent fraction of up to 90% in order to ensure a good metallic effect.

In the text below, the individual components of the mixer system of the invention will now be elucidated further.

20

Component A of the mixer system can contain all customary coatings pigments, with the proviso that they do not react with water within a very short time (period of time between the stirring of components A and B together and the application of the paints) and that they do not dissolve in water. Component A can comprise effect pigments and/or color pigments based on organic or inorganic substances. In order to ensure a scope for use which is as universal as possible and in

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order to be able to realize as many shades of color as possible, it is preferred to construct a mixer system on the basis of components A containing only color pigments and components A containing only effect  
5 pigments.

To prepare component A it is possible to use any effect pigments normally used in the formulation of aqueous coating compositions.

10

Examples of suitable effect pigments are commercial aluminum bronzes, the chromated aluminum bronzes of DE-A 36 36 183, commercial stainless steel bronzes, and other customary metal platelets and metal flake  
15 pigments. Also suitable for preparing component A are nonmetallic effect pigments, such as pearlescent pigments and interference pigments, for example.

Examples of suitable inorganic color pigments are titanium dioxide, iron oxides, carbon black, and the  
20 like. Examples of suitable organic color pigments are indanthrene blue, Chromophthal red, Irgazine orange, Sicotrans yellow, Heliogen green, and the like.

Suitable binders for use in component A include all  
25 water-dilutable or water-dispersible binders which are normally used in aqueous coating compositions and can be prepared in the form of organic solutions. The water-dilutability or water-dispersibility of the resins can also be adjusted by the use of corresponding

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solubilizers as a cosolvent or solvent. Critical to the selection of the binders is, on the one hand, good shelf stability in organic solution, including in particular the ability to avoid settling of the pigments, and, secondly, the ready ease of incorporation of the base color into component B or the ready ease of incorporation of component B into the base color. Although the ease of incorporation of the base color into component B and vice versa can be controlled through the use of dispersing additives, such as ionic or nonionic surfactants, for example, such additives should nevertheless be used in very small amounts in order not to impair the water resistance of the resulting coatings.

Binders used in particular for component A include water-dilutable or water-dispersible polyurethane resins, polyacrylate resins, polyester resins, and amino resins, which can be prepared in organic solution, and also mixtures thereof.

The polyurethane resins used as binders in the base colors are known in principle. Suitable examples include the polyurethane resins described in the literature for use in aqueous basecoat materials, provided these polyurethane resins - in modification of the preparation described in the respective literature - can be prepared in the form of organic solutions.

Examples of suitable polyurethane resins are the resins described in the following texts:

EP-A-355433, DE-A 3545618, DE-A 3813866, and the German  
5 patent application DE 4005961.8, which was unpublished at the priority date of the present specification.

For further details of the preparation of the polyurethane resins and examples of suitable compounds, therefore, refer to these texts. In contradistinction  
10 to the polyurethane resins described in these texts, however, the polyurethane resins are employed not as an aqueous dispersion but instead in solution in one or more organic solvents. This means that the preparation process of the polyurethane resins used in accordance  
15 with the invention has been altered in relation to the processes described in these texts, to the effect that, instead of the preparation of a secondary dispersion, the polyurethane resins are dissolved in organic solvents. It is preferred to use water-dilutable  
20 polyurethane resins which have a number-average molecular weight (determined by gel permeation chromatography using polystyrene as standard) of from 1 000 to 30 000, preferably from 1 500 to 20 000, and an acid number of from 5 to 70 mg KOH/g, preferably  
25 from 10 to 30 mg KOH/g, and are preparable by reaction, preferably chain extension, of prepolymers containing isocyanate groups.

The prepolymer containing isocyanate groups can be prepared by reacting polyols having a hydroxyl number of from 10 to 1 800, preferably from 50 to 1 200, mg KOH/g, with excess polyisocyanates at 5 temperatures of up to 150°C, preferably from 50 to 130°C, in organic solvents which are unable to react with isocyanates. The equivalents ratio of NCO groups to OH groups is between 2.0:1.0 and > 1.0:1.0, preferably between 1.4:1 and 1.1:1.

10

The polyols used for preparing the prepolymer can be low molecular and/or high molecular and can contain anionic groups which are slow to react. In order to increase the hardness of the polyurethane, low 15 molecular weight polyols can be used. They have a molecular weight of from 60 up to about 400 and can contain aliphatic, alicyclic or aromatic groups. Amounts of up to 30% by weight of the total polyol constituents, preferably from about 2 to 20% by weight, 20 are used.

In order to obtain an NCO prepolymer of high flexibility, a high fraction of a predominantly linear polyol having a preferred OH number of from 30 to 150 mg KOH/g should be added. Up to 97% by weight of 25 the total polyol can be composed of saturated and unsaturated polyesters and/or polyethers having a molar mass  $M_n$  of from 400 to 5 000. The selected polyetherdiols ought not to introduce excessive amounts



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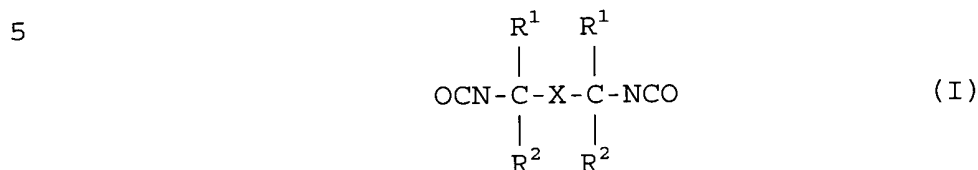
of ether groups, since otherwise the polymers formed undergo incipient swelling in water.

Polyesterdiols are prepared by esterification of  
5 organic dicarboxylic acids or their anhydrides with organic diols, or derive from a hydroxycarboxylic acid or a lactone. In order to prepare branched polyesterpolyols it is possible to a minor extent to use polyols or polycarboxylic acids having a higher  
10 functionality.

Typical polyfunctional isocyanates used include aliphatic, cycloaliphatic and/or aromatic polyisocyanates containing at least two isocyanate groups per molecule. The isomers or isomer mixtures of organic  
15 diisocyanates are preferred. Owing to their good resistance to ultraviolet light, (cyclo)aliphatic diisocyanates give products having a low tendency to yellow.

The polyisocyanate component used to form the  
20 prepolymer may also include a fraction of polyisocyanates of higher functionality, provided that this does not cause gelling. Products which have proven suitable as triisocyanates are products formed by trimerization or oligomerization of diisocyanates or  
25 reaction of diisocyanates with polyfunctional compounds containing OH or NH groups. The average functionality can be lowered if desired by adding monoisocyanates.

For preparing high-solids polyurethane resin solutions, use is made in particular of diisocyanates of the general formula (I)



10

in which X is a divalent, aromatic hydrocarbon radical, preferably an optionally halogen-, methyl- or methoxy-substituted naphthylene, biphenylene or 1,2-, 1,3- or 1,4-phenylene radical, with particular preference a 1,3-phenylene radical, and R<sup>1</sup> and R<sup>2</sup> stand for an alkyl radical having 1 to 4 carbon atoms, with particular preference a methyl radical.

Diisocyanates of the formula (I) are known (their preparation is described, for example, in EP-A-101 832, 20 US-A-3,290,350, US-A-4,130,577, and US-A-4,439,616) and are in some cases available commercially (1,3-bis(2-isocyanatoprop-2-yl)benzene, for example, is sold by the American Cyanamid Company under the trade name TMXDI (META)<sup>R</sup>).

25

In addition to diisocyanates of the formula (I) or instead of them it is also possible to use other aliphatic and/or cycloaliphatic and/or aromatic polyisocyanates. Examples of polyisocyanates which can 30 be used additionally include phenylene diisocyanate, tolylene diisocyanate, xylylene diisocyanate,

bisphenylene diisocyanate, naphthylene diisocyanate, diphenylmethane diisocyanate, isophorone diisocyanate, cyclopentylene diisocyanate, cyclohexylene diisocyanate, methylcyclohexylene diisocyanate, dicyclo-  
5 hexylmethane diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, hexamethylene diisocyanate, propylene diisocyanate, ethylethylene diisocyanate, and trimethylhexane diisocyanate.

10

Polyurethanes are generally incompatible with water unless specific constituents have been incorporated and/or special preparation steps taken during their synthesis. For preparing the polyurethane resins,  
15 therefore, it is possible to use compounds which contain two H-active groups which react with isocyanate groups, and at least one group which ensures dispersibility in water (carrier groups). Suitable carrier groups are nonionic groups (e.g., polyethers),  
20 anionic groups, mixtures of these two groups, or cationic groups.

Accordingly, it is possible to install in the polyurethane resin an acid number sufficiently great that the neutralized product can be dispersed stably in  
25 water. For this purpose, compounds are used which contain two H-active groups which react with isocyanate groups, and at least one group capable of forming anions. Suitable groups which react with isocyanate groups are, in particular, hydroxyl groups and also

primary and/or secondary amino groups. Groups capable of forming anions are carboxyl, sulfonic acid and/or phosphonic acid groups. Preference is given to using carboxylic acid or carboxylate groups. They should be sufficiently slow to react that the isocyanate groups of the diisocyanate react preferentially with the other groups in the molecule that are reactive toward isocyanate groups. For this purpose, use is made of alkanolic acids having two substituents on the  $\alpha$  carbon atom. The substituent can be a hydroxyl group, an alkyl group or an alkylol group. These polyols have at least one, generally from 1 to 3, carboxyl groups in the molecule. They have from two to about 25, preferably from 3 to 10, carbon atoms. The polyol contained carboxyl groups can make up from 3 to 100% by weight, preferably from 5 to 50% by weight, of the overall polyol constituent in the NCO prepolymer. The amount of ionizable carboxyl groups that is available as a result of the carboxyl group neutralization in salt form is generally at least 0.4% by weight, preferably at least 0.7% by weight, based on solids. The upper limit is approximately 6% by weight. The amount of dihydroxyalkanoic acids in the nonneutralized prepolymer gives an acid number of at least 5, preferably at least 10. At very low acid numbers, further measures are generally necessary in order to achieve dispersibility in water. The upper limit on the acid number is 70, preferably 40, mg KOH/g, based on solids.

The NCO prepolymers used in accordance with the invention can be prepared by simultaneous reaction of the polyol or polyol mixture with a diisocyanate excess. Alternatively, the reaction can be performed in  
5 stages in a prescribed sequence. Examples are described in DE A 26 24 442 and in DE A 32 10 051. The reaction temperature is up to 150°C, preference being given to a temperature in the range from 50 to 130°C.

The reaction is continued until virtually all of the  
10 hydroxyl functions have undergone reaction.

The NCO prepolymer contains at least about 0.5% by weight of isocyanate groups, preferably at least 1% by weight of NCO, based on solids. The upper limit is about 15% by weight, preferably 10% by weight, with  
15 particular preference 5% by weight.

If desired, the reaction can be conducted in the presence of a catalyst, such as organotin compounds and/or tertiary amines. In order to keep the reactants  
20 in the liquid state and to allow better control of temperature during the reaction, it is possible to add organic solvents which contain no Zerevitinov active hydrogen. The amount of solvent can vary within wide limits and should be sufficient to form a prepolymer  
25 solution of appropriate viscosity. In general from 10 to 70% by weight of solvents, preferably from 20 to 50% by weight of solvents, based on the solids, are used.

The isocyanate groups of the prepolymer that are still present are reacted with a modifier. This reaction leads in particular to further linking and increase in the molecular weight. The amount of said modifier is  
5 determined by its functionality and by the NCO content of the prepolymer. The ratio of equivalents of the active hydrogen atoms in the modifier to the NCO groups in the prepolymer should generally be less than 3:1 and preferably be in the range between 1:1 and 2:1.

10

Further modifiers used for reaction with the prepolymer include diols, with particular preference triols and/or polyols.

15 It is, however, also possible to use other compounds containing active hydrogen atoms as modifiers, examples being polyamines, albeit only with the proviso that the reaction of the prepolymer with the modifier can be carried out in an organic solvent (is controllable) and  
20 that this reaction is not accompanied by any unwanted reactions, such as the gelling at the point of dropwise addition of the amine that is often observed when using polyamines, for example.

Examples that may be mentioned of polyols contained at  
25 least three hydroxyl groups include trimethylolpropane, glycerol, erythritol, mesoerythritol, arabitol, adonitol, etc. Preference is given to using trimethylolpropane. The reaction of the prepolymer with the triols and/or polyols is preferably controlled via

the stoichiometry of the compounds used in such a way that chain extensions occur.

The polyacrylate resins used as binders for component A  
5 are likewise known and are described, for example, in DE-A 3832826. Suitable in general are water-dilutable and/or water-dispersible polyacrylate resins which can be prepared in the form of organic solvents.

10 Also suitable as binders for component A are water-dilutable and/or water-dispersible polyester resins which can be prepared in the form of organic solutions. Use is made, for example, of corresponding commercial, water-dilutable and/or water-dispersible polyester  
15 resins, and also of the polyester resins that are commonly used in aqueous basecoat materials.

Also suitable as binders for component A are water-dilutable or water-dispersible amino resins. It is  
20 preferred to use water-dilutable melamine resins. These are generally etherified melamine-formaldehyde condensation products.

Besides the degree of condensation, which should be as low as possible, the water-solubility of the amino  
25 resins depends on the etherifying component, with only the lowest members of the alcohol or ethylene glycol monoether series producing water-soluble condensates. The greatest importance is possessed by methanol-etherified melamine resins. When using solubilizers it

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is also possible to disperse butanol-etherified melamine resins in aqueous phase. A further possibility which exists is to insert carboxyl groups into the condensate. Transesterification products of highly  
5 etherified formaldehyde condensates with oxycarboxylic acids are water-soluble via their carboxyl groups, following neutralization, and can be present in the base colors.

10 As binders in the base colors A it is of course also possible to use mixtures of the aforementioned binders and also, in addition or alone, other water-dilutable or water-dispersible binders.

15 With preference, the binders present in the base colors A comprise water-dilutable polyurethane resins or water-dilutable amino resins or mixtures of water-dilutable polyurethane resins and amino resins.

20 As solvent, the base color contains one or more organic solvents. Examples of suitable solvents are, in particular, water-soluble or water-dilutable solvents, such as alcohols, esters, ketones, keto esters, glycol ether esters, and the like. Preference is given to  
25 using alcohols and glycol ethers, with particular preference butyl glycol and butanols.

It is possible here to use solvents during the actual preparation of the binders, these solvents also



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remaining later as solvents in the base color. More frequently, however, the binders are prepared using a different solvent, which following the preparation of the binders is distilled off gently by vacuum  
5 distillation or thin film evaporation and replaced by a solvent which remains in the binder solution that is then used in the base color. Relatively high-boiling solvents ought to be soluble in water, and remain in the polyurethane resin solution used in the base color  
10 in order to facilitate the coalescence of the polymer particles during film formation.

For example, the polyurethane resin solution is prepared in a ketone, such as methyl ethyl ketone or  
15 acetone. Following the addition of butyl glycol, solvent exchange takes place subsequently by distillative removal of the ketone (methyl ethyl ketone, acetone). Particularly preferred solvents for preparing the polyurethane resin are methoxypropyl  
20 acetate, ethoxyethyl acetate, and N-methylpyrrolone, which do not have to be replaced (no active hydrogen) and can remain in component A.

Where appropriate, these solvents for the preparation of the polyurethane resins can also be used in a  
25 mixture with ketones, although the ketones do not remain in the base color but are instead replaced after the polyurethane resin has been prepared.

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Component A may further comprise customary auxiliaries and additives. Examples of such additives are defoamers, dispersing aids, emulsifiers, leveling agents, and the like.

5

The preparation of component A takes place in accordance with methods known to the skilled worker, by mixing and, where appropriate, dispersing the individual components. Thus, color pigments are  
10 normally incorporated by grinding (dispersing) the respective pigments with one or more of the above-described binders, which are used preferably in the form of their solutions in organic solvents. Where appropriate, further organic solvent can be added for  
15 dispersing. Dispersing of these pigments is done using customary apparatus, such as bead mills and sand mills, for example.

The effect pigments are normally incorporated by mixing  
20 them homogeneously with one or more solvents. This mixture is then introduced with stirring into a mixture of one or more of the above-described binders, where appropriate with the addition of further organic solvents, by means of a stirrer or dissolver. The  
25 binders are used preferably in the form of their solutions in organic solvents.

As is familiar to the skilled worker, the respective proportions of pigment, binder, and solvent are guided

by the rheology of the pigment paste and are therefore dependent on the particular pigment used.

A further inventively essential constituent of the mixer system is the water-containing component B. It is conceivable to use a component B which contains only deionized water and thus serves only for adjusting the processing viscosity or processing solids of the base colors. Preferably, however, component B includes at least one rheology control additive. Where appropriate, component B may also contain further auxiliaries and additives, one or more water-dilutable and/or water-dispersible binders, and organic solvents.

Rheology control additives employed include crosslinked polymeric microparticles, as disclosed for example in EP-A-38127, and/or other customary rheological additives. Acting as thickeners, for example, are inorganic phyllosilicates, such as aluminum magnesium silicates, sodium magnesium phyllosilicates and sodium magnesium fluorine lithium phyllosilicates of the montmorillonite type, and also synthetic polymers containing ionic and/or associative groups, such as polyvinyl alcohol, poly(meth)acrylamide, poly(meth)-acrylic acid, polyvinylpyrrolidone, styrene-maleic anhydride or ethylene-maleic anhydride copolymers and their derivatives, or else hydrophobically modified ethoxylated urethanes or polyacrylates. It is preferred to use inorganic phyllosilicates as thickeners.

The sodium magnesium phyllosilicate is preferably used in the form of an aqueous paste. Particularly preferred pastes contain either 3% by weight phyllosilicate and 3% by weight polypropylene glycol or 2% by weight  
5 phyllosilicate and 0.6% by weight polypropylene glycol or 2% by weight phyllosilicate and 2% by weight other commercial surface-active substances, all percentages being based on the overall weight of the paste. These aqueous thickener pastes should be added only to  
10 component B and not to component A.

Suitable for use in component B are the water-dilutable or water-dispersible polyurethane, polyacrylate, polyester, and amino resins already listed in  
15 connection with the description of component A, so that here reference will be made only to pages 14 to 24 of the present description. In contradistinction to the use of these resins in component A, when used in component B these binders can be used not only as  
20 organic solution but also, preferably, in a water-containing form. This transfer of the resins to the aqueous phase takes place, for example, by neutralizing the carrier groups (groups capable of forming anions or cations, such as carboxyl groups, for example) and  
25 subsequently diluting them with water, where appropriate with partial removal beforehand of the organic solvent used in the preparation of the resin, or by direct synthesis of the resin in the presence of water. For further details refer to the literature

describing the preparation of the resins (cf., e.g.,  
DE-A 3210051, DE-A 2624442, DE-A-3739332,  
US-A 4,719,132, EP-A-89497, US-A 4,558,090,  
US-A 4,489,135, EP-A-38127, DE-A3628124, EP-A-158099,  
5 DE-A2926584, EP-A-195931, and DE-A3321180).

Also suitable as binders for component B are water-  
dilutable or water-dispersible polyurethane resins  
which cannot be prepared in the form of organic  
solutions. These are, in particular, polyurethane  
10 resins, where the prepolymer containing NCO groups was  
reacted with a polyamine modifier.

These polyurethane resins are normally prepared by  
first rendering the NCO prepolymer, described on pages  
15 14 to 22 of the present specification, dilutable with  
water or dispersible in water. For this purpose, for  
example, the anionic groups of the NCO prepolymer are  
at least partly neutralized using a tertiary amine.

20 The increase in water-dispersibility achieved by this  
means is sufficient for infinite dilutability. It is  
also sufficient to give a stable dispersion of the  
neutralized polyurethane. The isocyanate groups still  
present are reacted with the modifier. This reaction  
25 leads to further linking and increase in the molecular  
weight. Preferred modifiers are water-soluble  
compounds, since they increase the dispersibility of  
the polymeric end product in water. Organic diamines  
are suitable, since they generally build up the highest

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molar mass without gelling the resin. A prerequisite for this, however, is that the prepolymer is dispersed in water prior to chain extension or is present in some other sufficient dilution. The amount of modifier is  
5 determined by its functionality and by the NCO content of the prepolymer.

The presence of excess active hydrogen, particularly in the form of primary amino groups, can lead to polymers  
10 having an undesirably low molar mass. Chain extension can be carried out at least in part using a polyamine which has at least three amino groups containing a reactive hydrogen. This type of polyamine can be used in an amount such that, following the extension of the  
15 polymer, unreacted amine nitrogens with 1 or 2 reactive hydrogen atoms are present. Polyamines of this kind which can be used are diethylenetriamine, triethylenetetramine, dipropylenetriamine, and dibut-  
ylenetriamine. Preferred polyamines are the alkyl- or  
20 cycloalkyltrialamines, such as diethylenetriamine. In order to prevent gelling during chain extension, it is also possible to add small fractions of monoamines, such as ethylhexylamine.

25 Further suitable water-dilutable or water-dispersible binders for component B include the water-dilutable emulsion polymers which are described in DE-A3841540. These emulsion polymers are obtainable by

- a) in a first stage, polymerizing from 10 to 90 parts by weight of an ethylenically unsaturated monomer or of a mixture of ethylenically unsaturated monomers in aqueous phase in the presence of one or more emulsifiers and one or more radical-forming initiators, the ethylenically unsaturated monomer or mixture of ethylenically unsaturated monomers being selected such that in the first stage a polymer having a glass transition temperature ( $T_{g1}$ ) of from +30 to +110°C is obtained, and
- b) after at least 80% by weight of the ethylenically unsaturated monomer or monomer mixture used in the first stage have undergone reaction, in a second stage polymerizing from 90 to 10 parts by weight of an ethylenically unsaturated monomer or of a mixture of ethylenically unsaturated monomers in the presence of the polymer obtained in the first stage, the monomer used in a second stage or the mixture of ethylenically unsaturated monomers used in a second stage being selected such that polymerization of the monomer used in the second stage or of the mixture of ethylenically unsaturated monomers used in the second stage on its or their own would lead to a polymer having a glass transition temperature ( $T_{g2}$ ) of from -60 to +20°C, the reaction conditions being chosen such that the resulting emulsion polymer has a number-average molar mass of from 200 000 to 2 000 000,

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and the ethylenically unsaturated monomer or monomer mixture used in the first stage and the ethylenically unsaturated monomer or monomer mixture used in the second stage being selected in terms of their nature and amount such that the resulting emulsion polymer has a hydroxyl number of from 2 to 100 mg KOH/g, preferably from 10 to 50 mg KOH/g, and the difference  $T_{g1} - T_{g2}$  is from 10 to 170°C, preferably from 80 to 150°C.

10

The water-dilutable emulsion polymers used in accordance with the invention are preparable by a two-stage emulsion polymerization in an aqueous medium in the known apparatus by the known techniques.

15

The polymerization temperature is situated generally within the range from 20 to 100°C, preferably from 40 to 90°C. The quantitative ratio between the monomers and the water can be selected so that the resultant dispersion has a solids content of from 30 to 60% by weight, preferably from 35 to 50% by weight.

20

In the first stage it is preferred to use ethylenically unsaturated monomers or mixtures of ethylenically unsaturated monomers which are substantially free from hydroxyl and carboxyl groups. "Substantially free" is intended to denote that it is preferred to use monomers

25



or monomer mixtures which are free from hydroxyl and carboxyl groups but that the monomers or monomer mixtures used may also contain small amounts of hydroxyl and/or carboxyl groups (as a result of 5 impurities, for example). The amount of hydroxyl and carboxyl groups should preferably be not more than an amount which means that a polymer prepared from the monomer or monomer mixture used in the first stage has an OH number of not more than 5 mg KOH/g and an acid 10 number of not more than 3 mg KOH/g.

The emulsion polymer used in accordance with the invention ought to have a number-average molar mass (determined by gel permeation chromatography using polystyrene as standard) of from 200 000 to 2 000 000, 15 preferably from 300 000 to 1 500 000, and, normally, acid numbers of below 100 mg KOH/g and OH numbers of from 2 to 100 mg KOH/g. Where the emulsion polymer contains very few or no acid groups (acid number below about 3 mg KOH/g), it is advantageous to add a 20 carboxyl-containing resin, such as a carboxyl-containing polyurethane, polyester or polyacrylate resin, to the coating composition. The amounts of the carboxyl-containing resin are to be chosen such that the acid number of the mixture of emulsion polymer and 25 carboxyl-containing resin is greater than or equal to 10 mg KOH/g.

The skilled worker knows how he or she must choose the reaction conditions during the emulsion polymerization

in order to obtain emulsion polymers which have the number-average molar masses indicated above (cf., e.g., Chemie, Physik und Technologie der Kunststoffe in Einzeldarstellungen, Dispersionen synthetischer Hochpolymerer, Part 1 by F. Hölscher, Springer Verlag, 5 Berlin, Heidelberg, New York, 1969). The preparation of these water-dilutable emulsion polymers is described in detail in DE-A 3841540 on pages 2 to 5, so that here reference is made for further details simply to that 10 DE-A 3841540.

In addition, if desired, component B may comprise one or more organic solvents and also, where appropriate, further customary auxiliaries and additives. Examples 15 of suitable organic solvents are the solvents already listed in connection with the description of component A. The amount of organic solvent is normally from 0 to 3% by weight, based on the overall weight of component B. Examples of suitable auxiliaries and 20 additives are likewise the additives specified in connection with the description of component A. The amount in which these additives are used is normally from 0 to 10% by weight, based on the overall weight of component B.

25 If component B does comprise binders, preferred binders used are water-dilutable or water-dispersible polyurethane resins and/or amino resins or polyacrylate resins.

The mixer system of the invention for preparing aqueous coating compositions with precisely defined tinting is composed of different pigmented base colors (component A) and at least one water-containing component B. Depending on the desired shade of the aqueous coating composition, said aqueous coating composition is then prepared by mixing one or more base colors of the mixer system with at least one water-containing component B, directly prior to application of the aqueous coating composition. Typical mixer systems are composed of from 15 to 60, preferably from 20 to 40, different base colors, and from 1 to 5, preferably from 1 to 3, different components B.

As regards the description of customary mixing machines for stocking and storing the base colors and mixtures, reference is merely made to the literature, such as, for example, Glasurit-Handbuch, 11th edition, Kurt. R., Vincentz-Verlag, Hannover 1984, pages 544 to 547.

Preferred mixer systems of the invention are obtained using as component A base colors comprising

Aa) from 0.5 to 70% by weight of at least one effect pigment and/or at least one color pigment,

25

Ab) from 10 to 80% by weight of at least one water-dilutable or water-dispersible binder, and

Ac) at least one organic solvent,

the sum of the weight fractions of components Aa to Ac being in each case 100% by weight.

The base colors may further comprise from 0 to 10% by weight, based on the overall weight of component A, of customary auxiliaries and additives. With particular preference, the mixer system is composed of base colors which contain only effect pigments and base colors which contain only color pigments.

10

Particularly preferred base colors (component A) based on effect pigments comprise

15 Aa) from 0.5 to 50% by weight of at least one effect pigment,

Ab) from 20 to 80% by weight of at least one water-dilutable or water-dispersible binder, and

20 Ac) at least one organic solvent, the sum of the weight fractions of components Aa to Ac being in each case 100% by weight.

Particularly preferred base colors (component A) based on inorganic color pigments comprise

25

Aa) from 1 to 70% by weight of at least one inorganic color pigment,

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Ab) from 10 to 80% by weight of at least one water-dilutable or water-dispersible binder, and

Ac) at least one organic solvent, the sum of the  
5 weight fractions of components Aa to Ac being in each case 100% by weight.

In each case, a further constituent of component A is water in an amount of at least 5% by weight and less  
10 than 20% by weight, preferably from 6 to 19% by weight, most preferably from 8 to 16% by weight.

Particularly preferred base colors (component A) based on organic color pigments comprise  
15

Aa) from 1 to 30% by weight of at least one organic color pigment,

Ab) from 10 to 80% by weight of at least one water-dilutable or water-dispersible binder, and  
20

Ac) at least one organic solvent, the sum of the weight fractions of components Aa to Ac being in each case 100% by weight.

25

It is of course also possible as component A to use base colors which comprise a combination of at least one organic color pigment and at least one inorganic color pigment.

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As component B it is preferred to use mixtures which comprise

Ba) from 60 to 100% by weight, preferably from 80 to 97% by weight, of water,

5

Bb) from 0 to 10% by weight, preferably from 2 to 5% by weight, of at least one rheology control additive, this amount being based on the weight of the pure additive without solvent fraction, and

10

Bc) if desired, at least one water-dilutable or water-dispersible binder,

the sum of the weight fractions of components Ba to Bc being in each case 100% by weight.

15

For preparing the aqueous coating compositions, the different base colors A are mixed in a ratio such as to give the desired shade. The mixing proportion of component A with the component B or the different components B is determined by the requirement that, independently of the shade, the resulting coating composition has the desired viscosity, the desired solids content, and the desired amount of organic solvents, etc.

25

The solids content (amount of solid binder used plus amount of pigment used) and also the amount of organic solvent and the like varies with the intended use of

the aqueous coating compositions. In the field of automotive refinish paints, the solids content for metallic paints is preferably from 7 to 25% by weight and for straight-shade paints is preferably from 10 to 5 45% by weight, based in each case on the overall weight of the aqueous coating compositions.

One preferred embodiment of the mixer system of the invention is a mixer system in which all of the base 10 colors contain the same binder or, in the case of a binder mixture, the same binders. With particular preference, all of the base colors of the mixer system have the same ratio of the amount of solid binder (i.e., without solvent) used to the amount of organic 15 solvent used.

This ensures that, irrespective of the desired shade and thus irrespective of the mixing proportion of the different base colors, the resulting mixture of the different base colors always has the same 20 binder:solvent ratio and hence, irrespective of shade, exhibits an approximately consistent evaporation behavior (drying) and also a similar rheology. This constant binder:solvent ratio across all base colors further ensures that, where appropriate, the ratio of 25 binder (dissolved) to binder (dispersed) in the finished aqueous paint is also constant provided component B comprises binders.

If a mixture of different binders is used in each of the base colors, then the mixing proportion of the different binders with one another in the individual base colors ought preferably also to be constant in each case, so that, after mixing with component B, constant mixing proportions are again obtained in terms of the binders, irrespective of the shade. If in component B a mixture of the binders which are also used in component A is used, then in component B as well the mixing proportion of the different binders with one another ought preferably to be the same as the mixing proportion of these binders in component A.

Particularly preferred mixer systems are obtained if the base colors A comprise as binders water-dilutable polyurethane resins and, if desired, amino resin, and component B comprises as binders polyurethane resins. The aqueous coating compositions prepared using the mixer system of the invention can be applied to a very wide variety of substrates, such as metal, wood, plastic or paper, for example. The aqueous coating compositions prepared by means of the mixer system of the invention are suitable in particular for the refinish of damaged areas, particularly for automotive refinishing. In this case, the coating compositions, immediately following their preparation by mixing of components A and B, are applied to the appropriately prepared (e.g., by filling and surfacing) damaged area by means of customary methods, particularly spraying. With preference, the aqueous coating compositions



prepared using the mixer system of the invention are used to produce a basecoat film.

After the basecoat film prepared in this way has undergone partial drying at room temperature, or by means of forced drying (e.g., 10 min at 60°C, 80°C or IR drying), a suitable transparent topcoating composition is applied. Suitable topcoat material includes both organically dissolved and aqueous 1- or 2-component clearcoat materials and also powder clearcoat materials. Use is made frequently of 2-component clearcoat materials based on a hydroxyl-containing acrylate copolymer and a polyisocyanate. Clearcoat materials of this kind are described, for example, in the patent applications DE 34 12 534, DE 36 09 519, DE 37 31 652, and DE 38 23 005. Suitable 1-component clearcoat materials, based for example on a hydroxyl-containing binder and an amino resin curing agent, are likewise known and are described, for example, in Kittel, Lehrbuch der Lacke und Beschichtungen, volume IV; Verlag W.A. Colomb in der H. Heeremann GmbH, Berlin-Oberschwandorf 1976. Of course, however, all other clearcoat materials, not mentioned especially here, are suitable.

After a flashoff time, where necessary, of approximately 5 minutes, the basecoat film is then dried together with the topcoat film. When using 2-component clearcoat materials, drying takes place generally at temperatures of below 100°C, preferably

below 80°C. The dry film thicknesses of the basecoat are in general between 5 and 25  $\mu\text{m}$ , those of the topcoat generally between 30 and 70  $\mu\text{m}$ .

- 5 When using 1-component clearcoat materials, the basecoat film is dried together with the topcoat film at elevated temperatures, e.g., about 120°C. The dry film thicknesses of the topcoat in this case are generally between 30 and 50  $\mu\text{m}$ .
- 10 In the text below, the invention is illustrated with reference to working examples. All parts and percentages therein are by weight unless expressly stated otherwise.